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DIBAH-Reduction of the Diels-Alder Adducts of Buckminsterfullerene and Tropones: Formation of Derivatives Having Four Consecutive sp^3-Carbons

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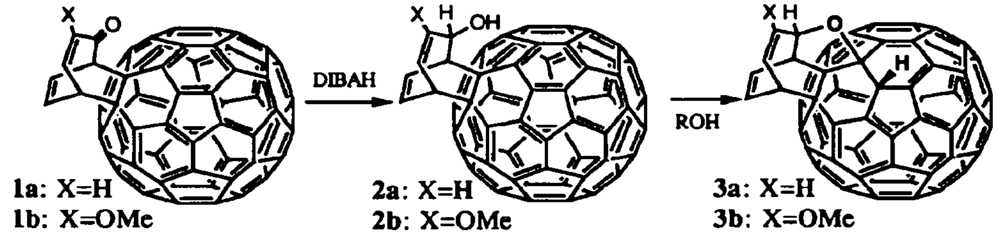
Abstract: By reduction with DIBAH, the high-pressure Diels-Alder adducts of buckminsterfullerene with tropone and 2-methoxytropone afforded dihydro derivatives. By standing these allyl alcohols at 15-20 °C in methanol, tetrahydrofuran derivatives were formed in good yields. The NMR spectral analysis established their full structures having unprecedented four consecutive sp^3-carbons. Same reduction of the adduct with 4-acetoxytropone afforded a tetrahydro derivatives, of which only the hydroxyl group on the three carbon bridge cyclized to form a tetrahydrofuran.

In view of an increasing interest on the cycloadditions of buckminsterfullerene (C_{60})[1] we have recently carried out a high-pressure Diels-Alder reaction between C_{60} and a series of tropone derivatives.[2] An acquisition of cycloadducts allowed us to investigate some chemical transformations with them. Herein described are the results of DIBAH (diisobutylaluminum hydride)-reduction and subsequent mild ring closure to tetrahydrofuran derivatives.



1a: X=H
1b: X=OMe

2a: X=H
2b: X=OMe

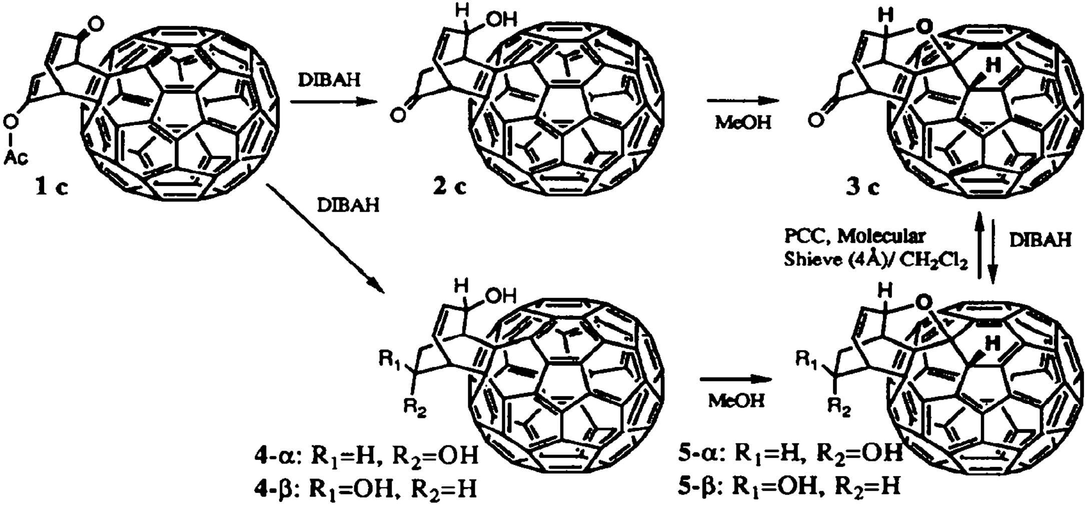
3a: X=H
3b: X=OMe

When a benzene solution of the Diels-Alder adducts (1a) of C_{60} and tropone was treated with DIBAH at 10 °C, under nitrogen atmosphere, a dihydro derivative (2a; IR ν 3450 cm^{-1}) was formed in 85% yield.

The ^{1}H NMR spectrum[3] of 2a assured it to be a 1,2-reduction product; a signal at δ=5.19, attributable to allylic methine proton, spin-coupled with the hydroxyl proton at δ=2.39(J=9.2 Hz). When 2a was kept in a methanol solution at room temperature for 2 h, new compound (3a; no IR ν_{OH} absorption) was formed in a 85% yield. Its ^{1}H NMR spectrum revealed a new singlet at δ=6.29, ascribable to a proton on the C_{60} skeleton, and the rest of proton signals showed a similar coupling sequences to those with 2a to assure the retention of the carbon framework; some characteristic differences were noticed, *e.g.*, the chemical shift differences on the etheno bridge carbons (Δδ) 0.26 in 2a changed to 0.61 in 3a with a considerable down field shift.

Interestingly, there is a positive NOE (3.5%) between the signals at δ=6.44, the signal ascribable to the proton on the vicinal to the ethereal carbon, and the above-mentioned signal at δ=6.29. The ^{13}C NMR spectrum revealed 62 over 67 possible signals; among them, newly formed sp^3-carbons of C_{60} moiety appeared at δ= 61.05 and 95.79, which showed couplings of *J*=139.72 and 8.73 Hz, respectively, with the proton signal at δ= 6.29 by SGNOE determination. Thus, the structure of **3a** has been established as depicted in the scheme. To the best of our knowledge, this is the first example of the compounds having four consecutive *sp^3*-carbons. Moreover, the tetrahydrofuran forming step constitutes a nucleophilic *cis*-1,2-addition of an alcohol to a condensed benzenoid system. Certainly, this type of the reactions should occur only with the very specific aromatics like fullerenes.

The adduct (**1b**), from 2-methoxytropone, similarly afforded a dihydro derivative (**2b**; IR(KBr) ν 3440 cm^{-1}), in 80% yield, and a tetrahydrofuran (**3b**; no IR ν_{OH} absorption), in 86% yield.



A brief DIBAH-reduction, 10 min at 10 °C, of an adduct (**1c**) from 4-acetoxytropone afforded a hydrolyzed dihydro keto alcohol (**2c**; IR(KBr) ν 3450 and 1730 cm^{-1}) in 32% yield, and an epimeric pair of tetrahydro derivative (**4**-α; IR(KBr) ν 3450 cm^{-1} and **4**-β; IR(KBr) ν 3450 cm^{-1}), in 40 and 18% yields, respectively. After prolonged period, all of **1c** was converted into **4**-α and **4**-β, 65 and 30% yields, respectively. Standing **2c** in methanol at room temperature afforded a similar tetrahydrofuran (**3c**; IR(KBr) ν 1720 cm^{-1}) in 60% yield. Also tetrahydro derivatives, **4**-α and **4**-β, gave isomeric tetrahydrofurans (**5**-α; IR (KBr) ν 3460 cm^{-1} and **5**-β; IR(KBr) ν 3450 cm^{-1}), both in 70% yields, respectively.[4] The ring-closure occurred only at the hydroxyl group on the three-carbon bridge. The DIBAH-reduction of **3c** also formed **5**-α and **5**-β in a same ratio.[5] An oxidation either **5**-α or **5**-β with pyridinium chlorochromate (PCC) in CH_2Cl_2 gave **3c** in good yield. It is interesting that the chemical shifts for epimeric methines on the oxygen-bearing carbon of **5**-α and **5**-β differ considerably, *i.e.*, δ=5.17 and 4.79, the latter of which should be assigned as the *exo*-hydrogen. It is predictable that the hydroxyl group on the two-carbon bridge is too distant to make an ethereal bond with a carbon on the framework, and this is reflected to enable the attack of hydride from the both sides.

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3. All the compounds are purified with HPCL (the conditions were described in ref. 2), and the NMR (in CDCl$_3$, otherwise specified, at 125 MHz for ^{13}C and 500 MHz for ^{1}H) features of some key compounds are herin recorded; for measurements of the ^{13}C NMR spectra, Cr(acac)$_3$ (0.035 M) were added as a relaxation agent, and underlined figures are carbon signals of the troponoid origin:

   2a (brown solid, dp 160 °C): δ(H)=2.39(OH, d, *J*=9.2 Hz), 4.43(1H, dddd, *J*=7.3, 2.6, 2.2, 1.1 Hz), 4.55(1H, ddd, *J*=8.4, 7.7, 1.1 Hz), 5.19(1H, dtd, *J*=9.2, 2.6, 2.2 Hz), 6.21(1H, ddd, *J*=11.0, 2.6, 2.2 Hz), 6.57(1H, ddd, *J*=11.0, 8.4, 2.2 Hz), 7.15(1H, ddd, *J*=8.8, 7.7, 1.1 Hz), and 7.41(1H, ddd, *J*=8.8, 7.3, 1.1 Hz). δ(C)=47.45, 56.21, 66.78, 73.29, 73.85, 130.97, 131.86, 132.56, 135.07, 136.10, 136.24, 137.07, 139.70, 140.13, 140.16, 140.21, 140.32, 141.56, 141.70, 141.72, 141.76, 141.83, 142.11, 142.13, 142.27, 142.31, 142.39, 142.49, 142.60, 142.70, 142.76(2C), 142.79, 143.31, 143.47, 144.67, 144.85, 144.87, 144.97, 144.99, 145.30, 145.41, 145.51, 145.53, 145.58, 145.59, 145.64, 145.73, 145.74, 145.76, 145.77, 145.85, 146.01, 146.34(2C), 146.50, 146.52, 146.59, 146.69(2C), 146.77, 147.84, 147.85, 155.54, 157.81, 158.12, and 159.12.

   2b (brown solid, dp 150 °C): δ(H)=3.12(OH, d, *J*=2.6 Hz), 3.83(3H, s), 4.54(1H, ddd, *J*=7.3, 2.6, 0.7 Hz), 4.55(1H, ddd, *J*=9.2, 7.7, 1.1 Hz), 5.08(1H, d, *J*=2.6 Hz), 5.63(1H, d, *J*=9.2 Hz), 7.12 (1H, ddd, *J*=8.8, 7.7, 1.1 Hz), and 7.44(1H, ddd, *J*=8.8, 7.3, 0.7 Hz). δ(C)=44.70, 52.73, 55.17, 66.52, 72.58, 73.64, 99.70, 130.32, 135.09, 135.65, 136.15, 137.34, 139.85, 139.97, 140.04, 140.13, 140.33, 141.45, 141.55, 141.62, 141.67, 141.84, 141.96, 142.08, 142.13, 142.15, 142.45, 142.48, 142.53, 142.57, 142.64, 142.72, 142.76, 143.17, 143.43, 144.69, 144.90, 144.94, 144.97, 144.99, 145.32, 145.36, 145.37, 145.44, 145.46, 145.49(2C), 145.50, 145.58, 145.65, 145.76, 145.87, 145.94, 146.24(2C), 146.36, 146.37, 146.47, 146.57, 146.61, 146.63, 147.74, 147.80, 156.19, 156.26, 158.14, 159.09, and 159.25.

   2c (brown solid, dp 150 °C): δ(H)=2.55(OH, d, *J*=8.8 Hz), 3.39(1H, br.d, *J*=18.0 Hz), 4.13-4.16 (1H, m), 4.20(1H, dd, *J*=18.0, 5.9 Hz), 4.70(1H, dd, *J*=8.1, 1.8 Hz), 5.30(1H, br.d, *J*=8.8 Hz), 6.53(1H, ddd, *J*=10.6, 8.1, 1.5 Hz), and 6.57(1H, dm, *J*=10.6 Hz).

   4-α (brown solid, dp 160 °C): δ(H)=2.37(OH, d, *J*=8.8 Hz), 2.44(OH, d, *J*=5.9 Hz), 3.26(1H, ddd, *J*=15.0, 10.3, 3.3 Hz), 3.41(1H, ddd, *J*=15.0, 7.0, 4.4 Hz), 3.86(1H, m), 4.05(1H, dm, *J*=9.5 Hz), 5.05(1H, ddm, *J*=10.3, 5.9 Hz), 5.25(1H, dtd, *J*=8.8, 2.6, 2.2 Hz), 6.43(1H, dt, *J*=10.6, 2.2 Hz), and 6.68(1H, ddd, *J*=10.6, 9.5, 2.2 Hz). δ(C)(CDCl$_3$/CS$_2$=5:1)=34.27, 52.23, 54.54, 64.80, 67.04, 71.17, 131.67, 134.04, 135.11, 135.80, 135.84, 135.94, 140.24, 140.37, 140.40, 140.41, 141.19, 141.41, 141.49, 141.66, 141.71, 141.94, 142.08, 142.20, 142.24, 142.27, 142.37, 142.61, 142.67, 142.73(2C), 142.76, 143.45, 143.46, 144.62, 144.66, 144.72, 145.03(2C), 145.11, 145.21, 145.24, 145.30, 145.53, 145.54, 145.64, 145.70, 145.71, 145.74(2C), 145.92(2C), 146.25, 146.29, 146.42, 146.47, 146.51, 146.52, 146.63, 146.65, 147.77, 147.82, 155.67, 156.45, 157.47, and 158.46.[6]

4-β (brown solid, dp 150 °C): δ(H)=2.20(OH, d, *J*=8.8 Hz), 2.34(OH, d, *J*=5.9 Hz), 2.46(1H, dd, *J*=17.6, 3.7 Hz), 3.87(1H, m), 3.88(1H, ddd, *J*=17.6, 9.5, 5.9 Hz), 4.30(1H, ddd, *J*=8.4, 5.9, 0.7 Hz), 5.28(1H, br.dm, *J*=8.8 Hz), 5.40-5.50(1H, m), 6.47(1H, ddd, *J*=10.6, 8.4, 1.8 Hz), and 6.58 (1H, dm, *J*=10.6 Hz).

3a (brown solid, dp 110 °C): δ(H)=4.13(1H, ddd, *J*=7.7, 5.1, 1.8 Hz), 4.57(1H, ddd, *J*=8.4, 7.3, 1.1 Hz), 5.54(1H, dd, *J*=5.1, 4.4 Hz), 6.29(1H, s), 6.44(1H, ddd, *J*=11.0, 4.4, 1.8 Hz), 6.67(1H, ddd, *J*=8.8, 7.7, 1.1 Hz), 6.99(1H, dd, *J*=11.0, 8.4 Hz), and 7.28(1H, dd, *J*=8.8, 7.3 Hz). δ(C)=48.93, 58.43, 61.02, 69.11, 71.32, 81.91, 95.79, 126.38, 129.42, 133.11, 136.38, 138.86, 139.28, 139.37, 140.90, 140.96, 141.12, 141.60, 141.79, 142.03, 142.37, 142.46(3C), 142.56, 142.74, 142.78, 142.86, 142.93, 143.06, 143.58, 143.84, 143.91(3C), 144.32, 144.38, 144.45, 144.52, 144.55, 144.63, 144.65, 144.81, 144.87, 144.93, 145.09, 145.42, 145.49, 145.68, 145.88, 146.43, 146.50, 146.56, 146.87, 146.91, 146.94, 147.49(2C), 148.27(2C), 148.37, 148.81, 148.91, 149.22, 151.83, 152.28, and 152.95.

3b (brown solid, dp 90 °C): δ(H)=3.94(3H, s), 4.20(1H, ddd, *J*=7.7, 5.5, 0.7 Hz), 4.56(1H, ddd, *J*=9.2, 7.3, 1.1 Hz), 5.43(1H, d, *J*=5.5 Hz), 5.95(1H, d, *J*=9.2 Hz), 6.12(1H, s), 6.66(1H, ddd, *J*=7.7, 7.3, 1.1 Hz), and 7.30(1H, td, *J*=7.3, 0.7 Hz). δ(C)($CDCl_3/CS_2$=3:1)=46.36, 55.02, 56.70, 60.43, 68.70, 71.75, 83.53, 96.06, 106.77, 125.40, 133.31, 136.44, 138.72, 139.22, 140.97, 141.01, 141.10, 141.70, 141.81, 142.39, 142.50, 142.55, 142.57, 142.67, 142.72, 142.78, 142.83, 142.91, 142.93, 143.01, 143.51, 143.79, 143.91, 143.97, 144.38, 144.40, 144.51, 144.55, 144.62(2C), 144.68, 144.83, 144.88, 144.94, 144.97, 145.15, 145.44, 145.52, 145.70, 145.88, 146.32, 146.50, 146.66, 146.80, 146.94, 147.00, 147.50, 147.55, 148.13, 148.41(2C), 148.83, 148.98, 149.28, 151.85, 152.27, 152.35, and 155.83.

3c (brown solid, dp 160 °C): δ(H)=3.34(1H, dd, *J*=20.5, 2.2 Hz), 3.50(1H, ddm, *J*=20.5, 6.2 Hz), 3.75(1H, dddd, *J*=6.2, 5.5, 2.2, 1.5 Hz), 4.64(1H, d, *J*=8.8 Hz), 5.67(1H, dd, *J*=5.5, 4.4 Hz), 6.26 (1H, s), 6.74(1H, dd, *J*=10.6, 8.8 Hz), and 6.87(1H, ddd, *J*=10.6, 4.4, 1.5 Hz).

5-α (brown solid, dp 150 °C): δ=2.21(OH, d, *J*=5.9 Hz), 2.72(1H, dt, *J*=16.1, 5.5 Hz), 3.15(1H, ddd, *J*=16.1, 10.3, 2.2 Hz), 3.49(1H, m), 4.13 (1H, dd, *J*=8.8, 2.2 Hz), 4.79(1H, dddd, *J*=10.3, 5.9, 5.5, 2.2 Hz), 5.51(1H, dd, *J*=5.5, 4.4 Hz), 6.18(1H, s), 6.70(1H, ddd, *J*=11.0, 4.4, 1.5 Hz), and 6.83 (1H, dd, *J*=11.0, 8.8 Hz).

5-β (brown solid, dp 150 °C): δ(H)=2.05(OH, d, *J*=6.6 Hz), 2.30(1H, ddd, *J*=15.8, 4.8, 1.1 Hz), 3.24(1H, ddd, *J*=15.8, 9.5, 7.7 Hz), 3.49(1H, ddm, *J*=7.7, 4.0 Hz), 4.24(1H, dd, *J*=7.7, 4.4 Hz), 5.17 (1H, dddm, *J*=9.5, 4.8, 6.6 Hz), 5.56(1H, dd, *J*=5.5, 4.0 Hz), 6.22(1H, s), 6.78(1H, dd, *J*=10.5, 7.7 Hz), and 6.86(1H, ddm, *J*=10.5, 5.5 Hz).

4. This tetrahydrofuran formation could not be completed due to an apparent equilibrium.
5. The interconversions, **5-α** and **5-β** to **3c**, has eliminated a possibility that **5-β** (the minor product) and **5-α** could be derived from isomeric Diels-Alder adducts, *i.e.*, a pair of regioisomers with a respect of 5/6- and 6/6-ring junctures, or that of *syn-* and *anti*-stereoisomers of 5/6-ring juncture. Should the Diels-Alder adducts be derived from 5/6-ring juncture, an exclusive formation of one isomer over another must be the least likely case.
6. One sp^3-carbon signal was hidden underneath the solvent signal.

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